

Behavior of block-polyampholytes near a charged surface

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Abstract

The behavior of polyampholytes near a charged planar surface is studied by means of Monte Carlo simulations. The investigated polyampholytes are overall electrically neutral and made up of oppositely charged units (called blocks) that are highly charged and of the the same length. The influence of block length and substrate's surface-charge-density on the adsorption behavior is addressed. A detailed structural study, including local monomer concentration, monomer mean height, transversal chain size, interface-bond orientation correlation, is provided. It is demonstrated that adsorption is favored for long enough blocks and/or high enough Coulomb interface-ion couplings. By explicitly measuring the chain size in the bulk, it is shown that the charged interface induces either a swelling or a shrinkage of the transversal dimension of the chain depending, in a non trivial manner, on the block length.

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I. INTRODUCTION

Polyelectrolytes (PEs, i.e., charged polymers) containing oppositely charged functional groups (blocks) are called polyampholytes (PAs). A well known example is provided by proteins (in particular gelatin). This class of material can be advantageously used as adsorbate and like that offer many applications in the every day life, such as paper production, dewatering [1], photographic films [2], etc.

In the last decade, many experimentalist researchers have investigated the adsorption behavior of PAs at charged substrates. For example, Neyret et al. [3] found that PAs with a negative net charge can adsorb onto negatively charged latex particles in accordance with the theoretical prediction of Joanny [4]. More recently, using silicon substrates Mahltig et al. [5, 6] studied the influence of the pH on the PA adsorption properties, where the net charge of the PAs can be tuned in a well controlled manner.

From a theoretical viewpoint, the behavior of PAs near a charged surface has been studied by various authors [4, 7, 8, 9]. Joanny [4] showed that PAs with non-zero net charge can adsorb on a surface that carries the same sign of electric charge for two distinct regimes: high and low screening strengths. Later, Dobrynin, Rubinstein and Joanny [9], using scaling law arguments, sketched typical adsorption regimes for salt-free environments. Based on a similar approach to that employed in Ref. [9], scaling theories were developed to elucidate the adsorption process of a single PA chain [7] and many PA chains on a charged sphere [8]. Shusharina and Linse [10] examined *grafted* diblock PAs at *uncharged* surfaces by a mean-field lattice theory and characterized the brush structure.

As far as computer simulations are concerned, only a few studies [11, 12] were devoted to the problem of PA adsorption. Akinchina et al. [12] performed Monte Carlo (MC) simulations on diblock PAs at uncharged spherical particles. The brush structure as a function of the charge ratio of the two blocks was examined [12]. Closely related to our problem, MC simulations were carried out by McNamara et al. [11] to characterize the molecular pattern recognition setting in upon adsorption of *sequenced* PEs (i.e., charge-ordered PAs or non-random PAs) to planar patterned surfaces. Using screened Coulomb interactions, they concluded that chain-entropy prevents efficient pattern recognition [11]. However, a detailed structural analysis and especially the monomer concentration profiles were not provided in Ref. [11] so that a clear description of the adsorption process of non-

random PAs onto charged surfaces is still missing. The fact that only patterned surfaces (checkerboards and stripes) were considered in Ref. [11] makes also the process of adsorption more specific and complicated.

The goal of this paper is to provide the mechanisms governing the adsorption of sequenced PEs (with a *zero* net charge) containing highly charged blocks onto charged planar surfaces. One can already anticipate and say that the overall chain adsorption properties are influenced by the following driving forces:

- (i) Chain-entropy tends to keep the chain in the solution.
- (ii) Electrostatic block-block correlations tend to collapse the chain into a globular form.
- (iii) A strong electrostatic interface-ion coupling favors chain adsorption.

We limit our study to the most simple situation where a single PA chain, whose blocks are equisized and carry the same magnitude of electric charge, interacts with a charged planar interface. That way, it should be easier to identify the relevant mechanics setting in PA chain adsorption. Computer simulations are especially useful in this regime of charge since most analytical theories [4, 7, 8, 9]. are only suitable for *weakly* charged blocks. Our article is organized as follows: The simulation model is detailed in Sec. II. Results are presented in Sec. III, and concluding remarks are provided in Sec. IV.

II. MODEL AND PARAMETERS

The model system under consideration is similar to that recently investigated for the adsorption of fully positively charged PEs [13, 14]. Within the framework of the primitive model we consider a *regular* polyampholyte near a charged hard wall with an implicit solvent (located at $z > 0$) of relative permittivity $\epsilon_r \approx 78$. To avoid the appearance of image forces [14] we suppose that the substrate (located at $z < 0$) below the interface (at $z = 0$) has the same dielectric constant.

The *negative* bare surface-charge density of the substrate's interface is $-\sigma_0 e$, where $e = 1.60219 \times 10^{-19} \text{C}$ is the (positive) elementary charge and σ_0 is the number of charges ($-e$) per unit area. The latter is always electrically compensated by its accompanying monovalent counterions of charge $Z_+ e$ (i.e., cations with $Z_+ = +1$) and diameter a . The block

PE corresponding to a perfectly regular polyampholyte is made up of $2N_b$ alternating positively/negatively charged blocks: Each block contains M monovalent charged monomers of the same sign of charge with a (typical) diameter a . Hence by construction the PA chain, containing altogether $N_m = 2N_b M$ charged monomers, is globally electroneutral. The corresponding counterions [i. e., monovalent anions ($Z_- = -1$) and cations] are also taken explicitly into account. Thereby, all the constitutive microions are monovalent and monosized with diameter a . All those particles are immersed in a rectangular $L \times L \times \tau$ box. Periodic boundary conditions are applied in the (x, y) directions, whereas hard walls are present at $z = 0$ (location of the charged interface) and $z = \tau$ (location of an *uncharged* wall). It is to say that we work in the framework of the primitive cell model.

The total energy of interaction of the system can be written as

$$U_{tot} = \sum_i \left[U_{hs}^{(intf)}(z_i) + U_{coul}^{(intf)}(z_i) \right] + \sum_{i,i < j} \left[U_{hs}(r_{ij}) + U_{coul}(r_{ij}) + U_{FENE}(r_{ij}) + U_{LJ}(r_{ij}) \right], \quad (1)$$

where the first (single) sum stems from the interaction between a microion i and the charged interface, and the second (double) sum stems from the pair interaction between microions i and j with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. All these contributions to U_{tot} in Eq. (1) are described in detail below.

Excluded volume interactions are modeled via a hardcore potential [15] defined as follows

$$U_{hs}^{(mic)}(r_{ij}) = \begin{cases} 0, & \text{for } r_{ij} \geq a \\ \infty, & \text{for } r_{ij} < a \end{cases} \quad (2)$$

for the microion-microion one, and

$$U_{hs}^{(intf)}(z_i) = \begin{cases} 0, & \text{for } a/2 \leq z_i \leq \tau - a/2 \\ \infty, & \text{otherwise} \end{cases} \quad (3)$$

for the interface-microion one.

The pair electrostatic interaction between two microions i and j reads

$$\beta U_{coul}^{(mic)}(r_{ij}) = Z_i Z_j \frac{l_B}{r_{ij}}, \quad (4)$$

where $l_B = \beta e^2 / (4\pi\epsilon_0\epsilon_r)$ is the Bjerrum length corresponding to the distance at which two charges e interact with $1/\beta = k_B T$. The electrostatic potential of interaction between a microion i and the (uniformly) charged interface reads

$$\beta U_{coul}^{(intf)}(z_i) = Z_i \frac{z_i}{\lambda}, \quad (5)$$

where $\lambda = \frac{1}{2\pi l_B \sigma_0}$ is the so-called Gouy-Chapmann length. The latter has two physical meanings: (i) It is the desorption length for an isolated ion of charge e (initially at contact with an oppositely charged wall) yielding an energy penalty of $k_B T$; (ii) It also corresponds (in the Poisson-Boltzmann theory) to the distance from the wall at which surface charges are half-compensated by their counterions. In order to characterize the electrostatic interface-ion coupling we consider the dimensionless “Moreira-Netz” parameter $\Xi = \frac{l_B}{\lambda}$ [16]. A modified Lekner sum was utilized to compute the electrostatic interactions with periodicity in two directions. To link our simulation parameters to experimental systems we choose $a = 4.25$ Å leading to the Bjerrum length of water $l_B = 1.68a = 7.14$ Å at $T = 298$ K.

The PA chain connectivity is modeled by a standard finite extendible nonlinear elastic (FENE) potential for good solvent, which reads

$$U_{FENE}(r) = \begin{cases} -\frac{1}{2}\kappa R_0^2 \ln \left[1 - \frac{r^2}{R_0^2} \right], & \text{for } r < R_0 \\ \infty, & \text{for } r \geq R_0 \end{cases} \quad (6)$$

with $\kappa = 27k_B T/a^2$ and $R_0 = 1.5a$. The excluded volume interaction between chain monomers is taken into account via a shifted and truncated Lennard-Jones (LJ) potential given by

$$U_{LJ}(r) = \begin{cases} 4\epsilon \left[\left(\frac{a}{r} \right)^{12} - \left(\frac{a}{r} \right)^6 \right] + \epsilon, & \text{for } r \leq 2^{1/6}a \\ 0, & \text{for } r > 2^{1/6}a \end{cases} \quad (7)$$

where $\epsilon = k_B T$. These parameter values lead to an equilibrium bond length $l = 0.98a$.

The equilibrium properties of our model system were obtained by using standard canonical MC simulations following the Metropolis scheme. In detail, single particle (translational) moves were applied to all the counterions (i.e., anions and cations) and the monomers with an acceptance ratio of 50%. For the sake of efficiency of the spatial sampling, we also apply

TABLE I: List of key parameters with some fixed values.

Parameters	
$T = 298K$	room temperature
$\sigma_0 L^2$	Numbers of charge ($-e$) on the substrate
$Z_{\pm} = \pm 1$	microion valence
$a = 4.25 \text{ \AA}$	microion diameter
$l_B = 1.68a = 7.14 \text{ \AA}$	Bjerrum length
$L = 35a$	(x, y) -box length
$\tau = 105a$	z -box length
M	number of monomer(s) per positive/negative block
$N_m = 64$	total number of monomers

time to time “global” translational displacements for the PA chain, where the *whole* chain is translated. The same acceptance ratio of 50% was applied there.

All the simulation parameters are gathered in Table I. The classes of the simulated systems can be found in Table II. For each class of systems characterized by a value of Ξ , we have systematically varied the block length M from 2 to 32 with intermediate values of $M = 4, 8, 16$, leading altogether to a set of 30 simulation runs. The monomer concentration is set to $c_m = \frac{N_m}{L^2\tau} \approx 4.976 \times 10^{-4}a^{-3}$ leading to a PA volume fraction $\phi = \frac{4\pi}{3}c_m(a/2)^3 \approx 2.605 \times 10^{-4}$ (see also Table I). The total length of a simulation run is set to $3 - 4 \times 10^6$ MC steps per particle. Typically, the first 10^6 MC steps were discarded, and about $2 - 3 \times 10^6$ MC steps were used to perform measurements.

III. RESULTS AND DISCUSSION

A. Preamble: Bulk behavior

Before evoking the problem of a PA at a charged interface, it is instructive to first consider the more simple bulk situation. To our knowledge, the influence of the length (M) of the charged block on the PA chain-size has not been systematically investigated in the literature. At all events, the understanding of the behavior of PA chains near a

TABLE II: Classes of simulated systems characterized by their value of $\Xi = \frac{l_B}{\lambda}$. The number of counterions (cations and anions) ensuring the overall electroneutrality of the system is not indicated. The symbol (\star) indicates *bulk* systems.

Ξ	$\sigma_0 L^2$
0 (\star)	0
0.9265	64
1.853	128
3.706	256
7.412	512

charged wall necessitates a knowledge of the limiting bulk system. To this end, we provide additional simulation data for the bulk situation (where $\Xi = 0$). Thereby, the PA chain and their counterions are placed in a spherical cell of radius $R_{cell} = 31.31a$ such that the monomer concentration $\frac{3N_m}{4\pi R_{cell}^3}$ remains identical to that studied in the slab geometry. The central $(N_m/2)^{\text{th}}$ monomer along the chain is held fixed and standard single particle moves as described above are applied. The duration of the simulation is set to 10^8 MCS leading to excellent statistics.

To characterize the chain conformation the radius of gyration defined as

$$\left\langle R_g^{(bulk)^2} \right\rangle = \frac{1}{N_m} \sum_{i=1}^{N_m} \langle (\mathbf{r}_i - \mathbf{r}_{cm})^2 \rangle \quad (8)$$

(where \mathbf{r}_{cm} designates the center of mass of the chain) was monitored. The results are presented in Fig. 1. Simulations show unambiguously that the chain shrinks with increasing block length M . This behavior is the result of an increasing cohesion between oppositely charged blocks with growing block charge. Similarly to what happens in an ionic crystal, upon increasing M one concomitantly enlarges the coordination number (i.e., the average number of neighbors of opposite charge). For longer chains, it is expected that the chain size should saturate from a certain threshold of M due to excluded volume effects. Some support to this latter statement seems to be provided by our simulations where the variation of the chain size is significantly slower at large values of M (see Fig. 1). Those preliminary findings will be useful to discuss our forthcoming results concerning the PA chain behavior near a charged interface.

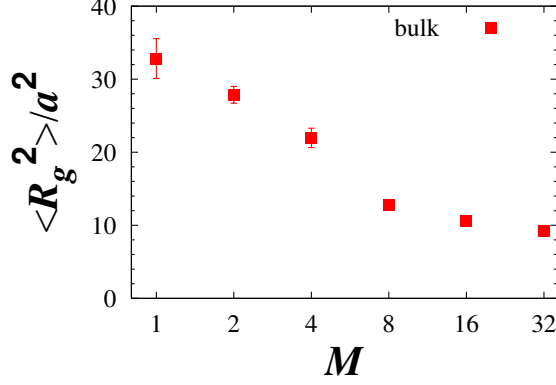


FIG. 1: Bulk mean square radius of gyration $\langle R_g^{(bulk)^2} \rangle$ as a function of the block length M .

B. Behavior at weak interface-ion Coulomb coupling

In this part, we focus on the situation where the interface-ion Coulomb coupling is weak (i.e., essentially $\Xi = 0.9265$). Since the interface is (negatively) charged and the chain is *flexible*, different behaviors are expected for the positively and negatively charged blocks, in contrast to what occurs in the bulk. It is important to have in mind that the role of the flexibility of the chain is crucial here, since the stiff version of our PA would lead to a conformation where the rod-like chain lies parallel to the normal z -direction of the interface (with one end touching the interface) in a minimal energy configuration.

To characterize the PA chain adsorption/depletion aspects, we have computed the monomer density profiles $n_{\pm}(z)$ defined as

$$n_{\pm}(z) = \sum_{i=1}^{N_m/2} \left\langle \delta \left(z - z_i^{(\pm)} \right) \right\rangle, \quad (9)$$

and normalized as follows

$$\int_{a/2}^{\tau-a/2} n_{\pm}(z) L^2 dz = \frac{N_m}{2}, \quad (10)$$

where $+$ ($-$) applied to positively (negatively) charged monomers. Our results are displayed in Fig. 2 and some microstructure snapshots are reported in Fig. 3. From a general viewpoint, the profiles of $n_{+}(z)$ and $n_{-}(z)$ in Fig. 2 are quite similar. The reason for that observation is (i) the connectivity between oppositely charged blocks and (ii) the weak Coulomb interface-block coupling. Those density profiles $n_{\pm}(z)$ exhibit a peak from $M \geq 4$ which is a signature of PA adsorption (see Fig. 2). The disappearance of a marked peak

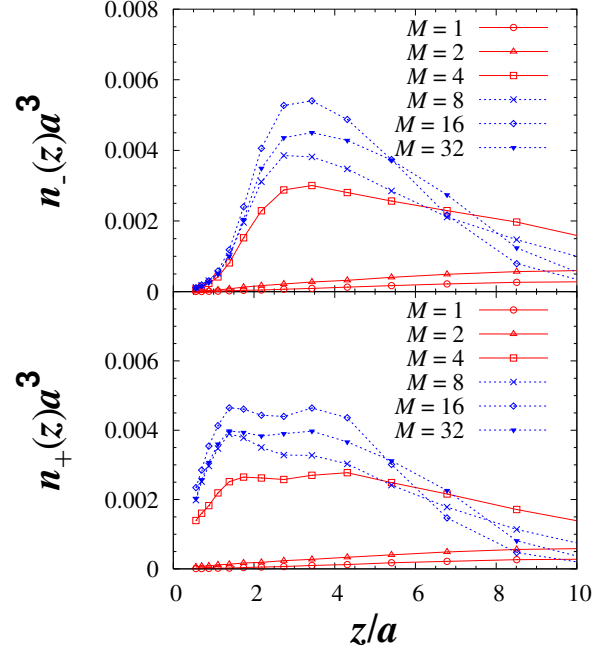


FIG. 2: Density profiles $n_{\pm}(z)a^3$ at $\Xi = 0.9265$ for various values of M .

in $n_{+}(z)$ can also be used as a criterion [17] for adsorption/depletion transition in our simulation. Such a criterion was utilized by Shafir et al. in their theoretical study of adsorption and depletion of polyelectrolytes from oppositely charged surfaces [18]. Near contact ($z/a \lesssim 1.5$) negatively charged monomers are strongly repelled from the wall due

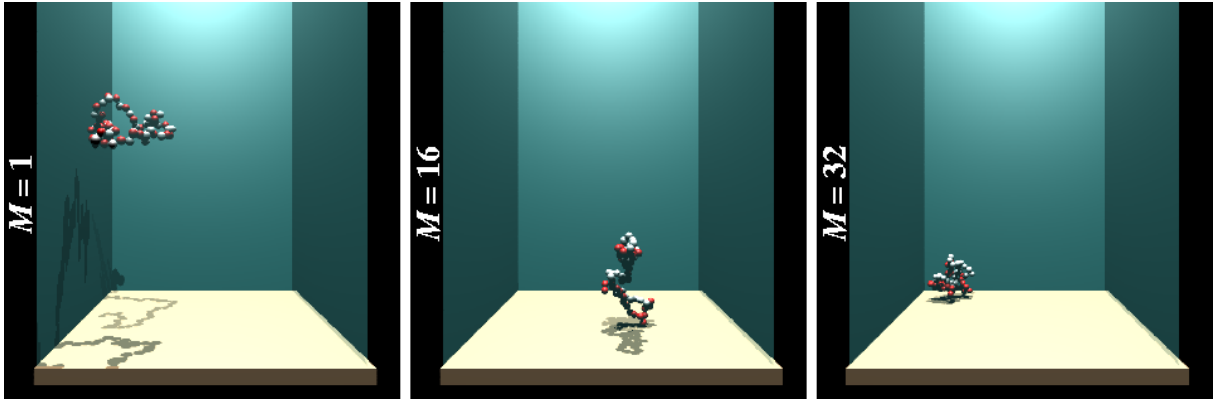


FIG. 3: Microstructure snapshots at $\Xi = 0.9265$ for block lengths $M = 1, 16, 32$ as indicated. The red (white) monomers correspond to positive (negative) charges. The little counterions are omitted for clarity.

to chain-entropy loss and wall-block electrostatic repulsion [see $n_-(z)$ in Fig. 2]. The positively charged monomers experience a short range repulsion as well but this time *only* due to chain-entropy effects [see $n_+(z)$ in Fig. 2]. This feature is well known for neutral chains [19], and was also reported by several authors for charged ones [13, 18, 20, 21]. The fact that the peak in $n_+(z)$ is considerably broadened (here at $M \geq 4$, see Fig. 2) suggests that the adsorption is rather weak. This statement will be justified later where larger Ξ coupling parameters are considered. It could be instructive to compare the contact value of $n_+(z \rightarrow a/2)$ to that obtain in the case where only the substrate's counterions are present [22] [i.e., the well known and *exact* contact value from the Gouy-Chapmann theory $n_c^{(GC)} = (2\pi l_B \lambda^2)^{-1} = \frac{\Xi^2}{2\pi l_B^3}$]. Introducing the dimensionless quantity ν defined as

$$\nu = \frac{n_+(z \rightarrow a/2)}{n_c^{(GC)}} = \frac{n_+(z \rightarrow a/2)}{\Xi^2 (2\pi l_B^3)^{-1}}, \quad (11)$$

Fig. 2 shows that a typical value of ν in the adsorption regime is roughly of the order of $\nu \approx \frac{0.002}{0.0288} \approx 0.07$. This low value confirms that the adsorption at $\Xi = 0.9265$ is (very) weak. Close to the wall ($z/a \lesssim 4$), Fig. 2 indicates that n_{\pm} increases systematically with M if the special *diblock* case ($M = 32$) is ignored. The non-trivial behavior at $M = 32$ is a result of a subtle competition between the interface-block interaction and the block-block correlations. The latter favor *non-flat* globular structures as well illustrated in Fig. 3 for $M = 32$. That effect can in turn lower the degree of adsorption and explain the non-trivial adsorption behavior reported in Fig. 2 at high N_m .

To further characterize the PA behavior at charged interfaces, we have measured the reduced mean height $\langle h_{\pm} \rangle$ defined as

$$\langle h_{\pm} \rangle = \int_{a/2}^{\tau-a/2} n_{\pm}(z) \frac{z}{a} L^2 dz, \quad (12)$$

where $+$ ($-$) applied to positively (negatively) charged monomers. Within this definition the mean height of the center of mass, $\langle h_{cm} \rangle$, corresponds to $\langle h_{cm} \rangle = \frac{\langle h_+ \rangle + \langle h_- \rangle}{2}$. $\langle h_{\pm} \rangle$ as a function of M (at $\Xi = 0.9265$) are reported in Fig. 4. One can distinguish two typical regimes (see Fig. 4): (i) At short charged blocks ($M = 1, 2$) the values of $\langle h_{\pm} \rangle$ are such that $\langle h_{\pm} \rangle \approx \frac{\tau}{2a}$ (within the statistical uncertainties) so that the chain is fully *delocalized* [23]. (ii) For longer blocks ($M \geq 4$), the mean heights decay by roughly one order of magnitude indicating an adsorption behavior that is consistent with the density profiles from Fig. 2.

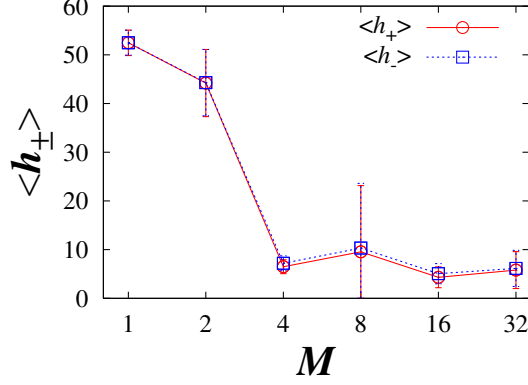


FIG. 4: Reduced mean heights $\langle h_{\pm} \rangle$ as a function of block length M

We now would like to address the problem of *desorption*. The term “desorption” generally means that some adsorbed substance gets released, which implicitly involves a dynamic process. For our present study, this latter feature can be best captured by monitoring the height of the monomers as a function of time. For that issue, we define the reduced height of positive charges, $h_{+}(t)$, as follows

$$h_{+}(t) = \frac{1}{a} \frac{\sum_i^{+} z_i(t)}{N_m/2}, \quad (13)$$

where the symbol “+” in the sum means that only positively charged monomers are counted.

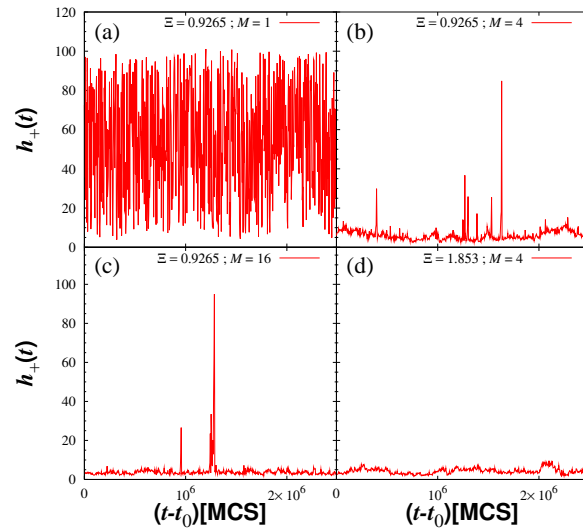


FIG. 5: Reduced height $h_{+}(t)$ as a function of time for different parameters as indicated. t_0 is a reference time.

The results for $h_+(t)$ for different set of parameters are shown in Fig. 5. The panels (a), (b) and (c) from Fig. 5 correspond to the lowest value of $\Xi = 0.9265$ whereas panel (d) corresponds to a higher value of $\Xi = 1.853$. The case of weakest interface-block coupling [i.e., $\Xi = 0.9265$ and $M = 1$, see Fig. 5(a)] shows large fluctuations of amplitude $h_+^{(max)} - h_+^{(min)} \sim \tau/a$ that are a dynamic signature of the delocalization, in agreement with the value of the static quantity $\langle h_+ \rangle \approx \frac{\tau}{2a}$ found in Fig. 4 for $M = 1$. Upon increasing the interface-block coupling (i.e., increasing M and/or Ξ), Fig. 5 indicates that the probability of escaping from the adsorbed state gets gradually weaker, as intuitively expected. The fact that at sufficiently high interface-block coupling the desorption processes become rare events, may in some cases considerably affect the quality of the statistical averaging as observed in Fig. 4 for $M = 8$. Consequently, a perfect equilibration is not always guaranteed for some parameters. Experimentalists are faced to the same problem when dealing with adsorption/desorption processes. This being said, we are confident that our simulations are reliable enough to capture the main qualitative features of the behavior of non-random PA chains at charged surfaces.

C. Behavior at intermediate and large interface-ion Coulomb coupling

In this part, larger interface-ion Coulomb couplings are considered corresponding to $\Xi = 1.853, 3.706$ and 7.412 (see Table II) with varying block lengths M . Many observables are going to be analyzed in detail and those can be classified into two main categories: (i) monomer concentration profiles and related quantities and (ii) chain conformation properties.

1. Monomer distribution

The monomer density profiles are depicted in Fig. 6. and some corresponding microstructure snapshots are sketched in Fig. 7. Let us first discuss the behavior of the positively charged monomers which is relevant for the adsorption, since without those no adsorption at all would occur. At $\Xi = 1.853$, the density profiles of the positively charged monomers exhibit similarity to that at $\Xi = 0.9265$ (compare Fig. 6 and Fig. 2), where especially the repulsive chain-entropy effects are present. An adsorption behavior is detected here for

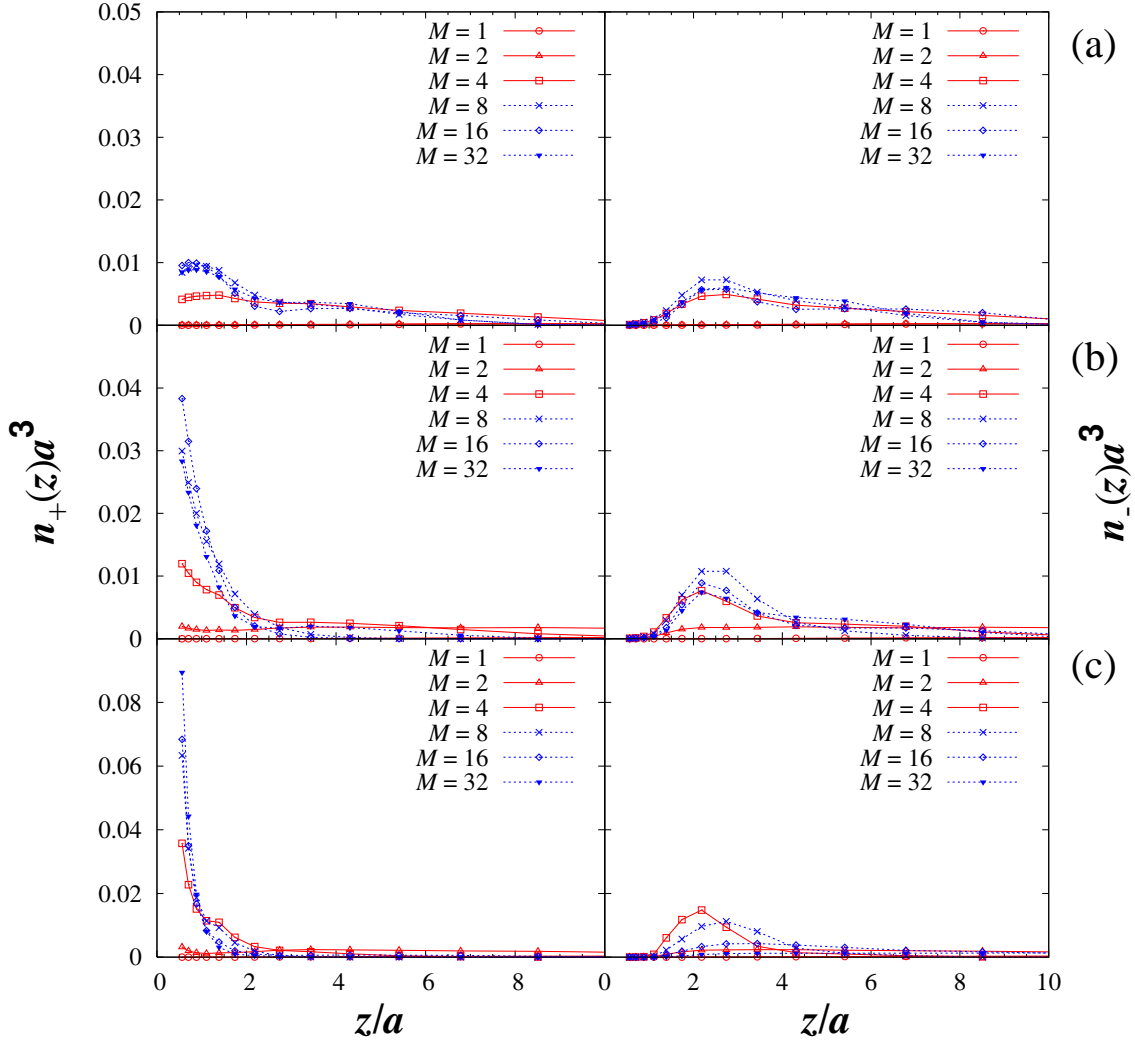


FIG. 6: Density profiles $n_{\pm}(z)^3$ for different block lengths M . The values of Ξ increase from top to bottom: (a) $\Xi = 1.853$ (b) $\Xi = 3.706$ (c) $\Xi = 7.412$.

$M \geq 4$ [see Fig. 6(a)]. This onset of adsorption can also be nicely visualized by comparing the snapshot of Fig. 7 (at $M = 4$ and $\Xi = 1.853$) to that of Fig. 3 (at $M = 1$ and $\Xi = 0.9265$) corresponding to the non-adsorbing case. However, at given M , more positively charged monomers can be found near the oppositely charged wall at $\Xi = 1.853$ than at $\Xi = 0.9265$ [roughly by a factor 2, compare Fig. 6(a) and Fig. 2]. At higher wall-ion couplings (i.e., $\Xi = 3.706$ and $\Xi = 7.412$), the scenario gets qualitatively different (see Fig. 6), where the $n_+(z)$ -profiles are now *monotonic* in contrast to what was found at $\Xi = 0.9265$ (see Fig. 2) and $\Xi = 1.853$. Physically, this means that the electrostatic effects overcome

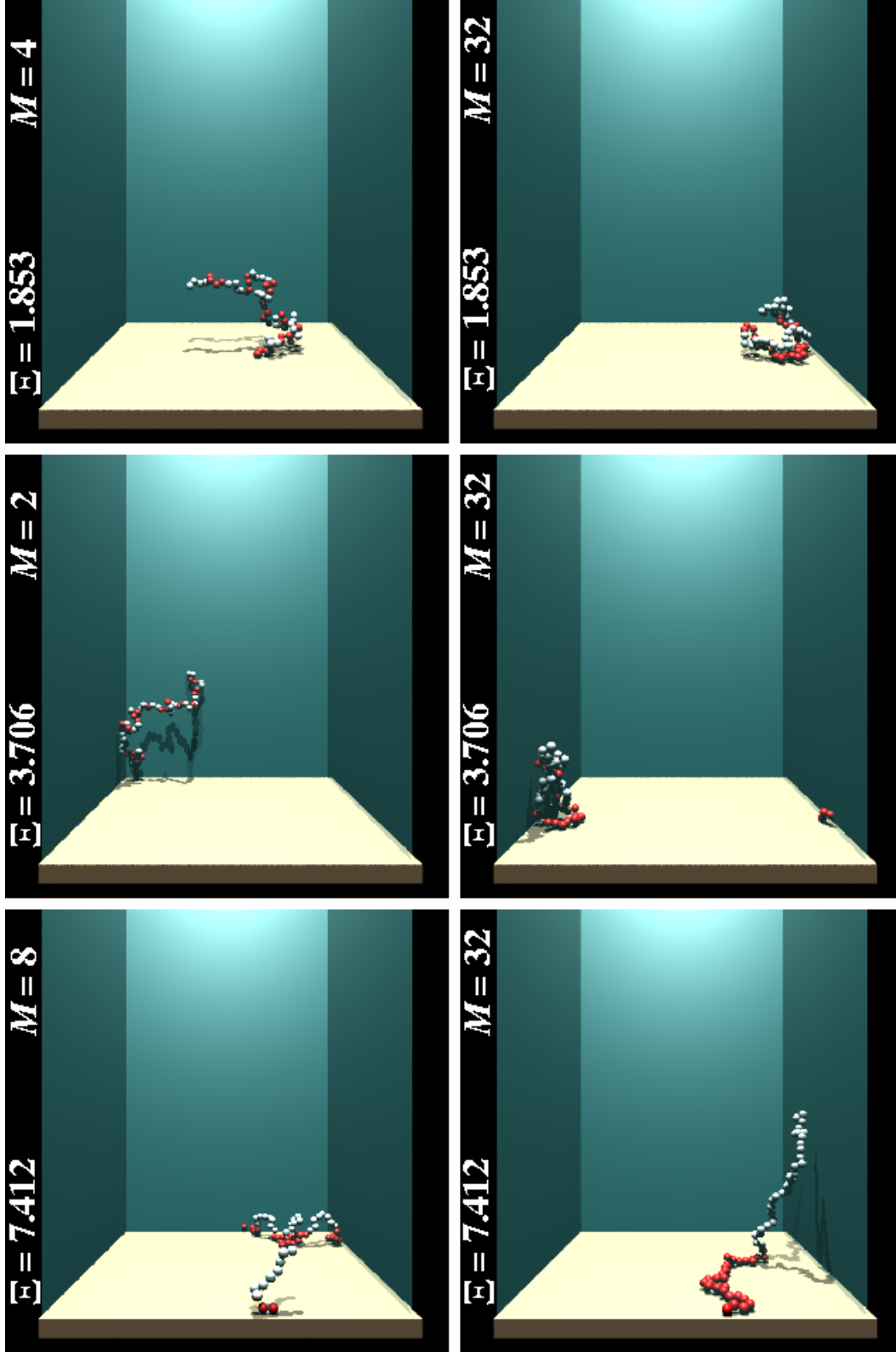


FIG. 7: Microstructure snapshots at different values of Ξ and M as indicated. Note that Ξ increases from top to bottom. The red (white) monomers correspond to positive (negative) charges. The little counterions are omitted for clarity.

the chain-entropy ones at sufficiently large Ξ . This feature can also be seen as signature of *strong* adsorption. A closer look at Fig. 6 reveals another interesting behavior, namely at our largest value of $\Xi = 7.412$, the density $n_+(z)$ near contact *increases systematically* with growing block length M , in contrast to what happens at lower Ξ (see also Fig. 2). This phenomenon can be explained by the strong wall-block electrostatic interaction that overcomes the cohesive block-block correlations. Those both effects grow with M in a non trivial way.

As far as the local concentration of negatively charged monomers $n_-(z)$ is concerned, Fig. 6 indicates a complicated behavior as a function of Ξ and M in the adsorption regime (here $M \geq 4$). More explicitly, at $\Xi = 1.853$ the maxima reached by $n_-(z)$ at long enough block length (here $M \geq 8$) are smaller than those of $n_+(z)$ [see Fig. 6(a)], in contrast to what was reported at $\Xi = 0.9265$ (see Fig. 2). This behavior is due to the stronger wall-block correlation existing at $\Xi = 1.853$. It is to say that the positively charged blocks get more attracted towards the negatively charged wall at higher Ξ and concomitantly the negatively ones get more repelled from it. The density profile $n_-(z)$ at $\Xi = 3.706$ is qualitatively similar to that obtained at $\Xi = 1.853$ (see Fig. 6), and a truly different behavior is found at $\Xi = 7.412$. There, in the strong adsorption regime (i.e., $\Xi = 7.412$ with $M \geq 4$), Fig. 6(c) interestingly indicates that only chains with intermediate block length $M = 4, 8$ can exhibit (significant) maxima in $n_-(z)$. The physical interpretation of this feature is that at high M the repulsion between the wall and the negatively charged blocks is so strong that, despite of the chain connectivity, the negatively charged get strongly repelled from the wall leading to formation of *loops* and *tails*. This mechanism explains also why $n_-(z)$, at $\Xi = 7.412$, is higher for $M = 4$ than for $M = 8$ in Fig. 6(c). All those relevant findings at $\Xi = 7.412$ are convincingly illustrated in Fig. 7 (at $\Xi = 7.412$) where a “*caterpillar*” structure is developed for $M = 8$, whereas a “L” structure rises for $M = 32$. Note that the former structure was also theoretically reported by Dobrynin et al. [9] for symmetric PAs that was referred to as the “pancake regime”. On the other hand, the “L” structure deserves some further comments. Naively one could think that solely the strong electrostatic interface-block interactions are sufficient to explain this structure. Basic electrostatics [24] show that this idea is wrong, and one must take into account the energy gain upon approaching the two oppositely charged blocks when passing from a stretched configuration (perpendicular to the interface) to the “L” structure. Hence, the “L” structure is again the result of interface-block interactions

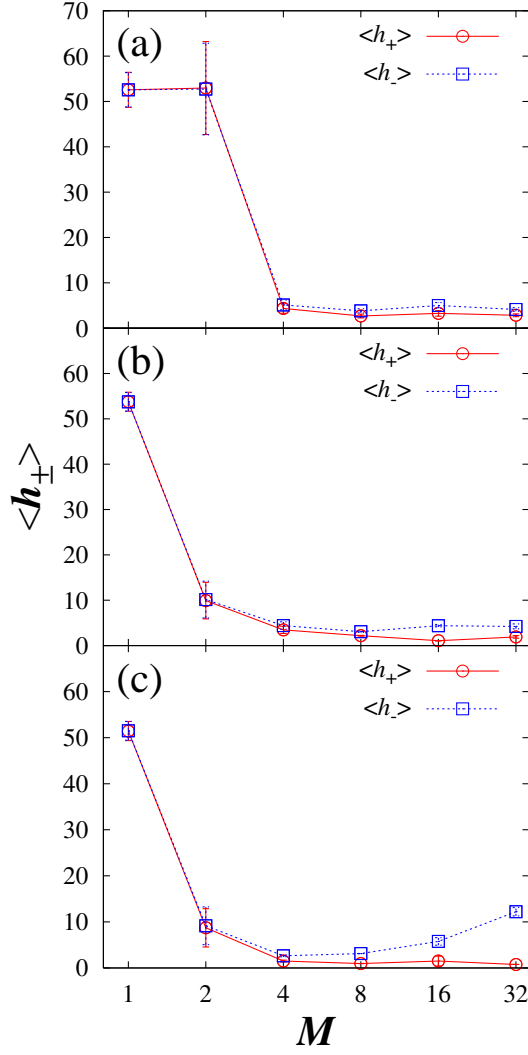


FIG. 8: Reduced mean heights $\langle h_{\pm} \rangle$ as a function of block length M for various values of Ξ increasing from top to bottom: (a) $\Xi = 1.853$ (b) $\Xi = 3.706$ (c) $\Xi = 7.412$.

and block-block correlations.

To gain further insight into the monomer distribution, we have plotted the mean heights $\langle h_{\pm} \rangle$ as a function of M in Fig. 8. For all values of Ξ , a *delocalized* state is reported at $M = 1$ as signaled by the value of $\langle h_{\pm} \rangle \approx \tau/2$ (see Fig. 8). That non-adsorption at $M = 1$ is due to the very weak polarizability of the chain there. The problem of chain polarization [see Eq. (14)] through the electric field stemming from the interface will be discussed in more detail later. Given that our highest value $\Xi = 7.412$ would correspond to $|\sigma_0 e| \approx 1e/(43\text{\AA}^2)$ (see also Table I for the chosen values of system parameters), which represents already the upper

limit of experimentally accessible surface charge densities, we expect that no adsorption should occur in reasonable experimental conditions when $M = 1$. At $M = 2$, only the case $\Xi = 1.853$ remains clearly delocalized (see Fig. 8). To rigorously assess the problem of localization/delocalization for the other remaining systems (especially for $M = 2$ at higher Ξ), a more appropriate investigation involving a systematic variation of the box height τ is required. Thereby if $\langle h_{\pm} \rangle \rightarrow \infty$ while $\tau \rightarrow \infty$, then the chain is said delocalized, otherwise it is localized. Noticing that $\langle h_{+} \rangle - \langle h_{-} \rangle$ represents the (reduced) *dipolar moment* $\langle p \rangle$ of the chain given by

$$\langle p \rangle = \left\langle \sum_{i=1}^{N_m} Z_i z_i \right\rangle = N_m \frac{\langle h_{+} \rangle - \langle h_{-} \rangle}{2}, \quad (14)$$

a closer look at Fig. 8 reveals (at given $M \geq 4$) that the adsorbed chain gets more and more polarized with increasing Ξ . The chain polarization is particularly vivid at high wall-block couplings where it increases with M [see Fig. 8(c)]. Concomitantly, this M -enhanced polarization effect yields a strong *non-monotonic* behavior for $\langle h_{-} \rangle$ at $\Xi = 7.412$ [see Fig. 8(c)]. Nonetheless, we stress the point that, in general for intermediate and weak ion-wall couplings Ξ , the polarization behavior as a function of M is non-trivial since $\langle p \rangle$ is also sensitive to the block-block correlations.

2. Conformational properties

A suitable quantity assessing the conformation of the chain is provided by the z -component $\langle R_{gz}^2 \rangle$ of the squared radius of gyration of the chain that is defined as follows

$$\langle R_{gz}^2 \rangle = \frac{1}{N_m} \sum_{i=1}^{N_m} \langle (z_i - z_{cm})^2 \rangle, \quad (15)$$

where z_{cm} designates the z -component of the center of mass of the chain. The square root $\sqrt{\langle R_{gz}^2 \rangle}$ can also be seen as the *thickness* of the chain in the adsorbed state. It is instructive to compare those values to those obtained in the bulk case (see Fig. 1). To this end, we introduce the following dimensionless quantity

$$\eta = \frac{\langle R_{gz}^2 \rangle}{\langle R_{gz}^{(bulk)^2} \rangle}, \quad (16)$$

where $\langle R_{gz}^{(bulk)^2} \rangle = \frac{1}{3} \langle R_g^{(bulk)^2} \rangle$. Thereby, $\eta < 1$ signals an interface-induced compression whereas $\eta > 1$ indicates an interface-induced stretching. Results for $\langle R_{gz}^2 \rangle$ are presented in

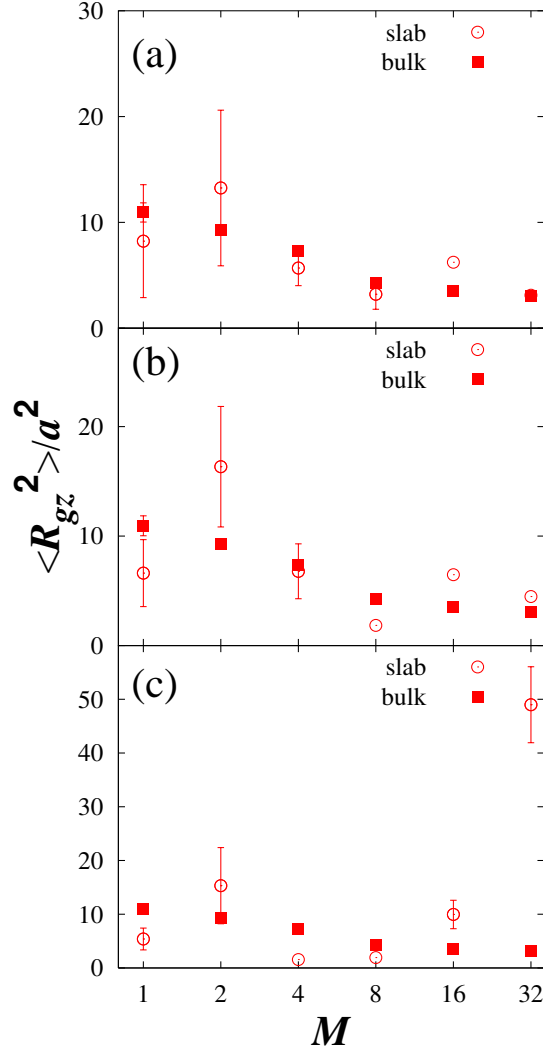


FIG. 9: Mean square radii of gyration $\langle R_{gz}^2 \rangle$ (slab) and $\langle R_{gz}^{(bulk)^2} \rangle$ (bulk) as a function of block length M for various values of Ξ increasing from top to bottom: (a) $\Xi = 1.853$ (b) $\Xi = 3.706$ (c) $\Xi = 7.412$.

Fig. 9. Despite of the rather large error bars appearing for the data points corresponding to the depletion/weak adsorption regimes, our simulations show that there is a systematic compression/stretching transition when passing from $M = 1$ to $M = 2$. This non-trivial phenomenon can be rationalized by considering the *stiff* limiting case. Indeed in the situation of a stiff rod-like PA, the minimal energy configuration (ignoring the counterions) would correspond to a chain “standing” on the wall with the positively charged end touching the interface, as previously discussed. Thereby, it is straightforward to show that the energy

gain increases with M (i.e., the dipolar moment of the chain). Hence at finite temperature, the rod-like will adopt an average orientation that gradually tends to be parallel to the z -direction when M is enlarged. Now, this idea can be qualitatively applied to flexible chains as long as the block-block correlations are not too strong, which is qualitatively the case for $M = 1, 2$ (see Fig. 1). Our scenario is perfectly illustrated by the snapshot in Fig. 7 at $\Xi = 3.706$ and $M = 2$. This stretching at $M = 2$ implies also larger values of $\langle R_{gz}^2 \rangle$ than at $M = 1$ (see Fig. 9). Note that this structure was also theoretically reported by Dobrynin et al. [9] for symmetric PAs that was referred to as the “pole regime”.

For longer blocks the situation is more complicated since there is a subtle competition between block-block correlations and block-wall ones. At intermediate block lengths ($4 \leq M \leq 8$) the chain is (again) in the compression regime (see. Fig. 9), whereas by further increasing M the chain gets stretched. A possible exception to this scenario is the diblock case ($M = 32$) at $\Xi = 1.853$ where $\eta \approx 1$ due to the strong block-block correlations and the rather weak interface-ion coupling there (see. Fig. 9). The “L” structure adopted by a diblock polymer chain at $\Xi = 7.412$ (see Fig. 7) leads to a strong stretching stemming from the negatively charged block (see. Fig. 9).

The chain conformation can be further characterized by evaluating the bond-wall orientation correlation. To quantify this order parameter we monitor the following second order Legendre polynomial

$$S_{\pm}(z) = \frac{\left\langle \sum_{i=1}^{N_{bond}} \frac{1}{2} \left[3 \left(\frac{\mathbf{b}_i^{(\pm)} \cdot \mathbf{e}_z}{|\mathbf{b}_i^{(\pm)}|} \right)^2 - 1 \right] \delta(z - \tilde{z}_i^{(\pm)}) \right\rangle}{\left\langle \sum_{i=1}^{N_{bond}} \delta(z - \tilde{z}_i^{(\pm)}) \right\rangle} \quad (17)$$

where $\mathbf{b}_i^{(\pm)} = \mathbf{r}_{i+1}^{(\pm)} - \mathbf{r}_i^{(\pm)}$ (with $\mathbf{r}_i^{(\pm)} = x_i^{(\pm)}\mathbf{e}_x + y_i^{(\pm)}\mathbf{e}_y + z_i^{(\pm)}\mathbf{e}_z$) stands for the bond vector linking only positively (+) charged monomers or only negatively (−) charged monomers, $N_{bond} = \frac{N_m(M-1)}{2M}$ is the total number of “positive” (or “negative”) bonds, and $\tilde{z}_i^{(\pm)} = \min(z_i^{(\pm)}, z_{i+1}^{(\pm)})$. Hence, $S_{\pm}(z)$ defined for $M \geq 2$ reaches the values $-\frac{1}{2}$, 0, and $+1$ for bonds that are perpendicular to the z -axis, randomly oriented, and parallel to the z -axis, respectively. Results for $S_{\pm}(z)$ are sketched in Fig. 10. Let us first analyze $S_+(z)$ where bonds link positively charged monomers. At contact ($z \lesssim a$), it can be seen from Fig. 10 that the positive bonds typically tend to lie the more parallel to the wall the larger the block

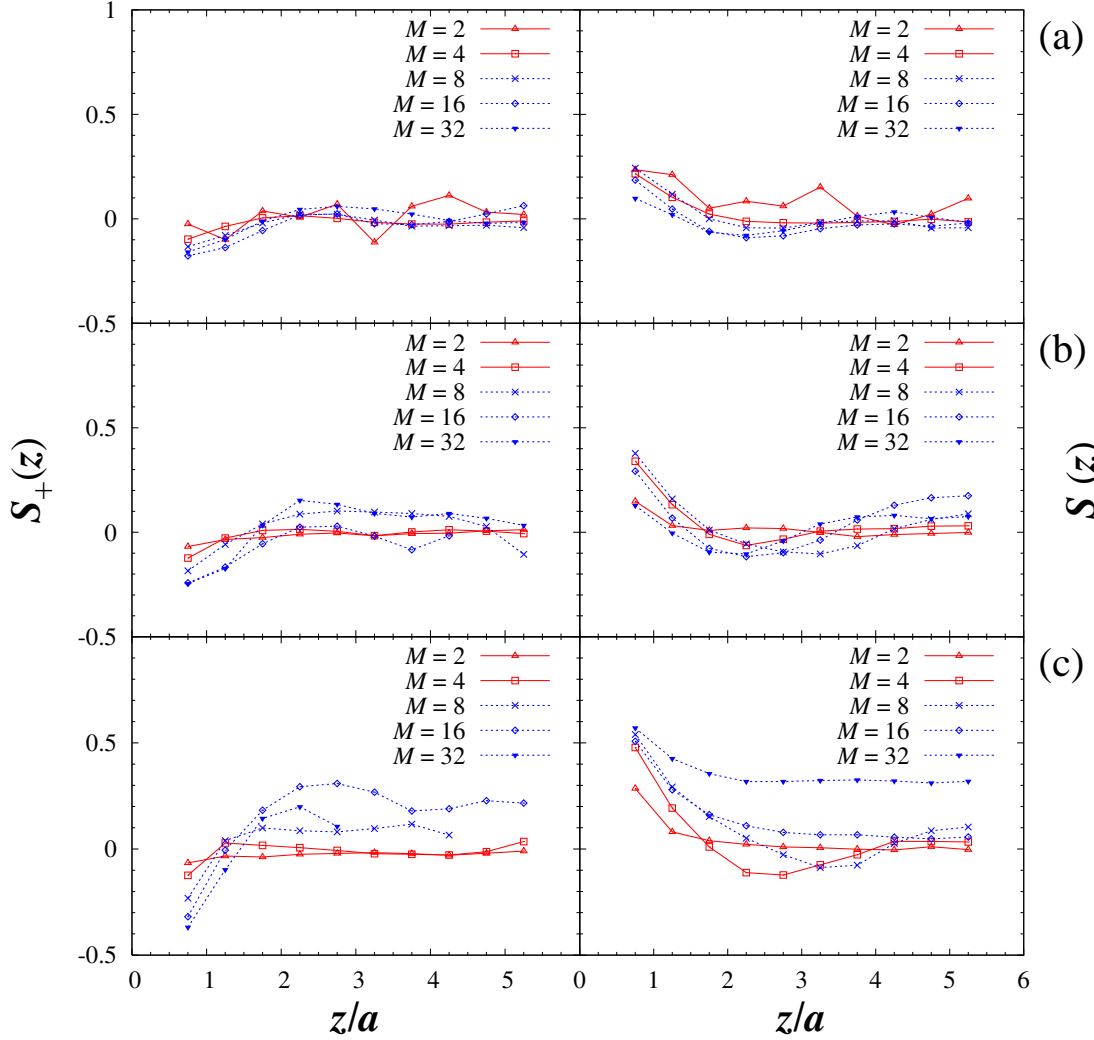


FIG. 10: Average bond-wall orientation correlation function $S_{\pm}(z)$ for different block lengths M . The values of Ξ increase from top to bottom: (a) $\Xi = 1.853$ (b) $\Xi = 3.706$ (c) $\Xi = 7.412$.

lengths, as signaled by negatively stronger values of $S_{+}(z)$. Moreover, the wall-bond degree of parallelism is enhanced when Ξ is increased at contact (see Fig. 10). Sufficiently far away from the wall, bonds get typically randomly oriented as signaled by a near 0 value reached by $S_{+}(z)$ (see Fig. 10). Nonetheless, in the regime of strong adsorption (i.e., $\Xi = 7.412$ and for $M \geq 4$), our simulation data show some deviation from that rule [see Fig. 10(c)]. This is merely due to the fact that at strong adsorption, positively charged monomers lying “far away” from the wall constitute rare events and therefore our results are not reliable for such high wall separations.

Concerning the bonds linking negatively charged monomers, an inspection of Fig. 10 reveals that the $S_-(z)$ -profiles can be seen qualitatively as the mirror reflexion of the $S_+(z)$ -profiles about the axis $S_\pm(z) = 0$. Still on a qualitative level, this mirror symmetry reflects simply the fact that positive bonds tend to get parallel to the wall whereas negative ones tend to stand perpendicular to the wall. This scenario is especially vivid at high $\Xi = 7.412$ as can be seen in Fig. 10(c) and in the snapshots from Fig. 7 taken at $\Xi = 7.412$. In particular, for the diblock case ($M = 32$), the snapshot [see Fig. 7(c)] reveals that the tail is stretched leading to a strong and *long-ranged* wall-bond orientation correlation with a typical correlation length that should be proportional to Ma .

IV. CONCLUDING REMARKS

We have presented a systematic set of MC simulations to address the behavior of a single flexible charge-ordered polyampholyte chain near a charged planar interface. The chain length was fixed and the constitutive blocks were highly charged with two consecutive blocks being oppositely charged. The influence of block length M and interface-ion Coulomb coupling Ξ on the overall chain conformation and adsorption properties were analyzed. Several relevant quantities were studied such as the local monomer concentration, the mean height of the centers of the positive and negative charges, the perpendicular component of the mean squared radius of gyration, the interface-bond orientation correlation function, and illustrative microstructural snapshots. Based on those results, our main findings can be summarized as follows:

- *No adsorption* occurs at monomer-sized blocks due to the weak chain polarization there.
- Chain adsorption can be obtained by increasing the *interface-block* coupling, i. e., increasing M and/or Ξ .
- By taking the bulk case as reference, compression-stretching transition sets in when passing from monomer-sized blocks to dimer-sized ones. The same behavior applies to the adsorption regime when passing from intermediate values of M to high values of M .
- Formations of tails and loops manifest only for strong interface-block couplings.

These findings can be possibly useful to provide some hints to recent experiments [5] where the (lateral) hydrodynamic diameter of adsorbed diblock polyampholytic structures on silicon substrates and that in the solution were measured by light scattering techniques. Consequently, the qualitative behavior of η [Eq. (16)] is experimentally specified (see Fig. 4 in Ref. [5]). Upon varying the pH Mahltig et al. [5] were able to gradually tune the net charge (from negative to positive passing through the isoelectric point) of the polyampholyte and that of the interface, and observed a similar compression-stretching scenario to that of our simulations.

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